Fluoride Adsorption by a Saline Sodic Soil Irrigated with a High F Water*

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Summary. Langmuir isotherm data for F adsorption were obtained from 1 : 10 soil : water extracts of soil samples from a lysimeter study. A sodic silt loam surface soil with a saline sodic subsoil was irrigated with a high sodium chloride, high fluoride (0.38 mMF) geothermal well water. A previous study showed that fluorite (CaF_2) was precipitated from solution in the upper portion of this profile while another mechanism removed F solution in the lower part of the profile to below 0.02 mMF. The Langmuir isotherm data indicate that one kind of surfaces or sites remove fluoride from solution over the 0 to 1.1 to 1.2 mMF range. The adsorption capacity for this F removal is about 4.4 to 5.8 mmol F/kg of soil and the equilibrium constant is between 0.54 to 1.00 l/mmol F. Once these surfaces or sites were saturated, a second kind of sites removed F from solution, and had an adsorption capacity of 9.2 to 11.4 mmol/kg and an equilibrium constant of 0.16 to 0.27 l/mmol. Both data sets fit the Langmuir equation. At some point before or after this second set of sites or surfaces was saturated, the fluorite ion activity product was exceeded and fluoride was then removed from solution via fluorite precipitation. The two adsorption mechanisms lowered the soil solution F concentration sufficiently to prevent ground water contamination, but once the adsorption sites were saturated, fluorite precipitation does not decrease F concentration sufficiently to meet drinking water standards.

Many deep aquifers and geothermal waters in the western United States contain high fluoride (F) concentrations (0.2 to 1.0 mMF) (Kubota et al. 1982; Rowe et al. 1973). This concentration is higher than the 0.1 mMF (2 mg F/kg) generally considered acceptable for human or livestock drinking water. Considerable information is available in the literature concerning F reactions in acid and neutral soils

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but only limited information is available for calcareous and sodic soils (Bower and Hatcher 1966; Gupta et al. 1982). In arid and semiarid areas where water is in short supply, many high F waters are being developed for irrigation on soils with pH values over 7.5. Irrigation with high F, geothermal power plant waste water on high pH soils has also been proposed as a disposal alternative in arid and semiarid areas. This suggestion has caused concern that the F from these waters might eventually leach into shallow aquifers used for domestic and livestock drinking waters.

In a previous study 6 lysimeters filled with 0.7 m of saline sodic subsoil and 0.3 m of sodic surface soil and irrigated at 0.15 and 0.30 leaching fractions, retained over 98% of the applied F when irrigated with a high F geothermal well water (Tracy et al. 1984). The water contained 0.38 mMF (7.2 mg F/kg) and had an EC of 2.7 dS/m. From 6 to 26 pore volumes of water drained from the bottoms of the lysimeters.

An alfalfa (*Medicago sativa* L. 'Ranger') barley (*Hordeum vulgare* L. 'Steptoe') mix was planted. After the barley matured and was harvested, the alfalfa was maintained to concentrate the soil solution salts and F by evapotranspiration. At the end of the study the lysimeters were sampled at 0.1 m increments and analyzed for Ca, Mg, Na, K, SO_4, Cl, HCO_3, F, pH, and EC in saturation paste extracts. The fluorite (CaF_2) ion activity product and total amounts of soluble Ca and F were back calculated to the 24% moisture basis (0.03 MPa soil water potential) to determine if CaF_2 was precipitating and if so, how much. Between 12 and 21% of the applied F was calculated to be in the CaF_2 form, and less than 3% of the applied F was measured in the leachate. The rest was unaccounted for.

Bower and Hatcher (1966) found that over the range of 0–1.0 mMF, F adsorption could be described by the linear form of the Langmuir equation in six soils (some had been acid washed to remove the lime) and nine clay minerals. These F concentrations are considerably lower, however, than those in the soil solutions of Tracy et al. (1984), since the irrigation water initially contained 0.38 mMF and this solution was concentrated in the soil 3.3 to 6.7 times by evapotranspiration.

In soil columns irrigated with high F waters (0–260 mMF) Flühler et al. (1982) found that the F breakthrough curves, shape and time depended primarily on the F concentration and soil type while ionic composition had only minimal effect. The F retention in their soil columns could be estimated from 1 : 10 soil : water isothermal adsorption data for an acid soil but the calcareous soils retained only ⅓ to ½ as much F as would be predicted by the isotherm data. They also found that quartz sand adsorbed very little if any F from solution.

When comparing pH and exchangeable sodium percentage (ESP) effects on F adsorption by alkaline soils from India, Gupta et al. (1982) found that as the pH increased, F adsorption decreased, while ESP increases at a constant pH had very little effect on F adsorption.

The purpose of this study was to determine whether the F that had not been accounted for in the previous study had been removed by a reaction that could be described by the Langmuir adsorption model.

Methods

Soil samples from the two lysimeters that had received the 30% leaching fraction irrigations in the previous study (Tracy et al. 1984) and samples of the untreated surface soil and subsoil used to fill the lysimeters were used for this study. The 15% leaching fraction data from the previous study are not shown here due to the close similarity to the presented data. Triplicate ten gram samples from each 0.10 m depth sample increment was equilibrated with 100 ml solutions containing from 0 to 5.26 mMNaF/L (100 mg F/kg). The solution total ion concentration was maintained constant by adding sufficient NaCl to the NaF solution to maintain a total 5.26 mM solution. The 1 : 10 soil : solution suspensions were shaken in a constant temperature bath ($25 \pm 0.5\,^{\circ}C$) for 24 h. The suspension pH was measured and the samples were centrifuged. A 25 ml sample of the supernatant was added to 25 ml of buffer solution, shaken, and the F concentration was measured with a combination F electrode. The total ionic strength adjustment buffer (TISAB) contained 1.0 mol each of acetic acid and NaCl and 4 g of (1,2-Cyclohexylenedinitrite)-tetraacetic acid per liter, adjusted to pH 5.0–5.5 with NaOH. The "soil solution equilibrium F concentration" was determined as the concentration at which F was neither sorbed nor desorbed from the NaF-NaCl solution by the soil sample (Table 1, Column 2).

Adsorption isotherms for the samples were also plotted using the linear form of the Langmuir equation:

$$\frac{C}{x/m} = \frac{1}{Kb} + \frac{C}{b}, \tag{1}$$

where C in the solution F equilibrium concentration, x/m is the mM of F adsorbed per unit mass (kg) of adsorbent. K is a constant and is a function of the binding strength and b is the maximum amount of adsorbate that can be adsorbed by a particular mechanism (Bohn et al. 1979). Values for K, b, and r, the correlation coefficient of the individual data points in relation to the line fitted to these points for the plots, were tabulated for these samples which fit the Langmuir equation· (Table 1, Columns 4–9).

Results and Discussion

In the previous study (Tracy et al. 1984), fluoride concentrations in 1 : 10 soil : distilled water extracts varied from less· than 0.05 mMF in the lower half of the lysimeters to over 1.6 mMF in the surface 0.4 m of the profile. Ion activity products in the upper profile were in the range one would expect to find if fluorite (CaF_2) were present in the solid phase. The leachate initially contained 0.03 to 0.07 mMF but rapidly dropped to below 0.02 mMF after the second leaching event. From 77 to 87 percent of the applied F could not be accounted for in the leachate or the soluble CaF_2 form. Most crops, including alfalfa, do not remove significant amounts of F from the soil solution and can be ignored as a F sink (Kubota et al. 1982).

The first phase of this study was to determine the solution F concentration required in a 1 : 10 soil : water suspension that would be in equilibrium with the

Table 1. 1:10 Equilibrium concentrations, pH and adsorption capacities, equilibrium constants and r values for first and second Langmuir isotherms for soils used to fill lysimeters and soil samples at end of study

Soil Sample	1:10 equil.		First isotherm			Second isotherm		
	mM/l	pH	Adsorp. cap. mM/kg	Equil. const. K/mM	r	Adsorp. cap. mM/kg	Equil. const. K/mM	r
Surface soil	0.08	8.9	2.22	0.85	0.980	5.43	0.25	0.999
Sub soil	0.13	10.00	1.72	0.75	0.996	3.27	0.33	0.998
Lysimeter A								
0.0–0.1 m	1.60	7.9						
0.1–0.2 m	2.81	8.1						
0.2–0.3 m	4.47	8.4						
0.3–0.4 m	5.09	8.7						
0.4–0.5 m	2.73	9.1						
0.5–0.6 m	0.15	9.2	5.72	0.79	0.996	11.44	0.23	0.996
0.6–0.7 m	0.11	9.2	5.83	0.88	0.985	9.63	0.25	0.978
0.7–0.8 m	0.11	9.2	5.88	1.00	0.997	9.43	0.18	0.995
0.8–0.9 m	0.13	9.1	4.67	0.92	0.999	11.02	0.23	0.989
0.9–1.0 m	0.10	9.3	5.71	0.54	0.994	11.10	0.20	0.993
Lysimeter B								
0.0–0.1 m	1.41	7.8						
0.1–0.2 m	2.63	8.3						
0.2–0.3 m	3.33	8.3						
0.3–0.4 m	5.34	8.7						
0.4–0.5 m	1.79	8.9						
0.5–0.6 m	0.20	9.2				11.41	0.17	0.995
0.6–0.7 m	0.12	9.1	6.08	0.68	0.982	10.66	0.16	0.955
0.7–0.8 m	0.10	9.1	5.38	0.73	0.990	10.01	0.27	0.999
0.8–0.9 m	0.09	9.2	4.66	0.71	0.986	9.24	0.21	0.990
0.9–1.0 m	0.13	9.0	4.44	0.88	0.993	10.35	0.26	0.995

sorbed phase (regardless of the form), wherein F would neither be removed from or added to the liquid phase by the solid phase. This is in contrast to the 1 : 10 soil : distilled water extract as described in the previous fluorite precipitation study. In the upper profile 1 : 10 equilibrium concentrations ranged from 1.4 to 5.34 mMF and below 0.5 m the concentrations decreased rapidly to below 0.20 mMF (Table 1, Column 2). The 1 : 10 soil : water extract solution pH values are shown in the third column for all samples.

The 1 : 10 soil : water fluoride values were plotted according to Eq. (1) for samples from that portion of the profile where $C/x/m$ increased with increases in extract equilibrium solution F concentration.

The F adsorption data were plotted for the original soils and the 0.8 to 0.9 m depth increment from the two lysimeter irrigated at 30% leaching fraction (Fig. 1). Adsorption data from the other two lysimeters showed the same trend. All samples from 0.5 to 1.0 m deep in the profile were very much like the two lower curves
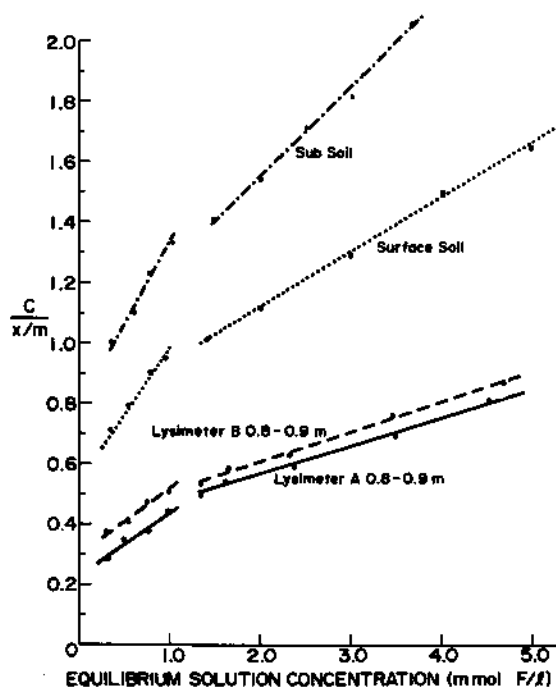
Fig. 1. Linear Langmuir isotherm plots of the untreated surface and subsurface soil used in the lysimeters and of the 0.8–0.9 m depth increment samples at the end of the study

shown. This is reflected in the adsorption capacity and equilibrium constant values (Table 1). Above 0.5 m, where CaF_2 appears to have precipitated, the data did not produce the straight lines, but produce negative values for $C/x/m$ at extraction solution concentrations below that required to keep CaF_2 from dissolving.

When adsorption conforms to the Langmuir model, a plot of $C/x/m$ versus C is a straight line with a slope of $1/b$ and an intercept of $1/Kb$. K which is obtained by dividing the slope by the intercept is a constant related to the adsorption energy and is shown in Table 1 as the equilibrium constant K. The reciprocal of the slope, b, is the adsorption capacity of a particular reaction and is expressed in this case as mMF/kg of soil.

In the upper profile samples, fluorite was assumed present (Tracy et al. 1984) and consequently the data did not produce a straight line. Below the CaF_2 precipitation zone, two distinct kinds of F adsorption appear to have taken place. When F solution concentration was less than about 1.1 to 1.2 mMF, the adsorption constant K was between 0.54 and 1.0 l/mM. At equilibrium concentrations above 1.2 mMF, K decreased to below 0.27, suggesting that a second kind of site was adsorbing F which did not hold the F nearly as tightly (Table 1, Columns 3–8). At concentrations below the break in the two lines, 4.44 to 6.08 mmol F could be adsorbed per kg soil by the first site or mechanism, while 9.24 to 11.44 mmol F could be adsorbed per kg of soil by the second kinds of sites at higher concentrations. Data for the untreated soils produced nearly the same K values but much lower capacity values. This result can be attributed to decreases in pH values caused by irrigation and leaching (Gupta et al. 1982). The untreated soils also

exhibited the two site Langmuir model. The Langmuir values shown in Table 1 for the deeper depths after leaching were quite similar to those obtained by Bower and Hatcher (1967) for their calcareous soils that had not been acid washed.

Under the conditions of this study where high pH soils were irrigated with 0.38 mMF water, F appeared to be removed from soil solutions by adsorption and precipitation. Initially, a set of adsorption sites were active over the range of 0 to 1.1 or 1.2 mMF and removed F until those sites were saturated. At that point a second kind of adsorption took over. Somewhere along the line, before or after the second mechanism was saturated, the fluorite ion activity product was exceeded and CaF_2 precipitated from solution. The two adsorption mechanisms can lower F in percolating water to levels acceptable for drinking water standards. However, once these sites are saturated, fluorite precipitation will not lower F concentrations sufficiently in calcareous soils to protect shallow aquifers from F pollution. These soils have a finite upper limit for F removal from percolating irrigation water by adsorption, but probably an infinite capacity to remove F as CaF_2, thus, the deep drainage water F concentration will eventually be controlled by Ca ion activity which in turn is controlled by several other factors (Robbins 1985).

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